Journal of Alloys and Compounds 495 (2010) 506–508

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Non-equilibrium cation influence on the Néel temperature in $ZnFe_2O_4$

S.J. Stewart [a,*], I.A. Al-Omari [b], F.R. Sives [a], H.M. Widatallah [b]

[a] IFLP, CCT-La Plata, CONICET and Departamento de Física, Facultad de Ciencias Exactas, C. C. 67, Universidad Nacional de La Plata, Calle 49 y 115, 1900 La Plata, Buenos Aires, Argentina
[b] Physics Department, Sultan Qaboos University, PO Box 36, 123 Muscat, Oman

ARTICLE INFO

Article history:
Received 31 July 2008
Received in revised form 28 October 2009
Accepted 29 October 2009
Available online 10 November 2009

Keywords:
Néel temperature
Ferrites
Zinc ferrite
$ZnFe_2O_4$

ABSTRACT

We present results on the thermal dependence of the magnetization above ambient conditions of $ZnFe_2O_4$ nanoferrites having different degrees of inversion ($c \sim 0.05$–0.40) and grain sizes ($D \sim 6$–50 nm). The disordered ferrites present a net magnetization in the 400–510 K range that mainly depends on the degree of inversion. The reciprocal magnetization deviate from different temperature values of the linear behavior showed at high temperatures. Our results show that, contrary to similar nanoferrite systems, a simple scaling law cannot be applied to explain the Néel temperature T_N dependency with the grain size. These results can be interpreted in terms of the lack of correlation between size and inversion that occurs in $ZnFe_2O_4$ and the strong T_N dependence on the superexchange J_{AB} interaction strength. A model assuming a random distribution of superexchange interactions can reproduce the Curie–Weiss temperature and the saturation magnetization values of the disordered ferrites.

1. Introduction

The antiferromagnetic (AF) ordering that occurs in normal $ZnFe_2O_4$ at the Néel temperature $T_N = 10$ K has been attributed to Zn^{2+} and O^{2-} defects rather than to its intrinsic behavior [1]. In any case, the AF configuration is driven by J_{BB} superexchange interactions between Fe^{3+} ions at octahedral B sites since the totality of diamagnetic Zn^{2+} ions are preferentially located at tetrahedral A sites. Numerous works have reported that nanosized $ZnFe_2O_4$ presents a non-equilibrium distribution of cations where Zn^{2+} and Fe^{3+} occupy both A and B sites [2–4]. This gives rise to J_{AB} interactions that changes its long range ordering to a ferrimagnetic one with $T_N \sim 460$–490 K [3,5]. A T_N of about 120 K was reported for $ZnFe_2O_4$ nanoparticles of 20 nm, although in this case it is difficult to distinguish whether it actually corresponds to the Néel temperature or to the blocking temperature of the particle moments [6]. Studies related to the magnetism of disordered $ZnFe_2O_4$ have been mainly focused on its low temperature behavior and, to our knowledge, only one work has reported on its magnetization above ambient conditions [5]. However, the exploration of the magnetic behavior of disordered ferrites above room temperature can provide useful information for some ferrite applications. For instance, potential hyperthermia applications might require the control of T_N that guarantees a ferrimagnetic response a few tens of degrees above room temperature [7].

We present here an investigation about the temperature dependence above room temperature of the magnetization of $ZnFe_2O_4$ nanoferrites having different degrees of inversion and sizes. Our results and others from the literature are compared with theoretical predictions by assuming a random distribution of superexchange interactions.

2. Experimental

Nanocrystalline $ZnFe_2O_4$ (2ZF) was obtained by a hydrothermal procedure. Samples 2ZF4H and 2ZF10H were obtained after high energy ball milling (HEBM) 2ZF for 4 and 10 h [4]. Nanostructured ferrite (BZF10H) was obtained by HEBM bulk $ZnFe_2O_4$ for 10 h. The milling was carried out in a horizontal miller with a stainless steel vial and ball (mass to powder ratio of 10:1). Sample 2ZF10H-T was obtained after annealing 2ZF10H under oxygen flow from ambient up to 673 K (during 60 min), 773 K (60 min) and 873 K (120 min).

X-ray diffraction (XRD) patterns were taken in a Philips PW 1710 diffractometer (CuKα, $\lambda = 1.5406$ Å). Grain sizes, D, were estimated by using Scherrer's equation considering the most intense Bragg peak, i.e., the line (3 1 1) (Table 1). X-ray absorption spectra (XANES and EXAFS) at Zn and Fe K edges were collected at room temperature in transmission mode at the XAS beamline of the LNLS, Campinas, Brazil [4,8]. Magnetic measurements in the 298–610 K range were carried out using a commercial vibrating sample magnetometer under a 10 kOe magnetic field. Additional magnetic measurements were taken using a superconducting quantum interference device magnetometer and an AC susceptometer.

3. Results and discussion

The X-ray diffraction studies showed that all the samples consist of $ZnFe_2O_4$ cubic spinel. The grain sizes D are shown in Table 1 [4,8]. The degree of inversion, c, defined as fraction of iron ions at site A, was estimated from EXAFS data [4,8] (Table 1).

---

[*] Corresponding author. Tel.: +54 221 4246064x243; fax: +54 221 4252006.
E-mail address: stewart@fisica.unlp.edu.ar (S.J. Stewart).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.10.258

Table 1
Grain size D, inversion parameter c, ordering temperature T_N, Curie–Weiss temperature θ_W, blocking temperature T_B and saturation magnetization M_S at 5 K for the described sample.

Sample	D (nm)	c	T_N (K)	θ_W (K)	T_B (K)	M_S (emu/g)
2ZF	6	0.22	395	285	38	35
2ZF4H	9	0.31	427	405	135	57
2ZF10H	13	0.38	444	465	265	68
BZF10H	14	0.40	518	502	307	72
2ZF10H-T	50	0.05			37	

Fig. 1 shows the hysteresis loops taken at room temperature. We observe that no matter HEBM is causing an increment or a reduction of the grain size, it always produces an enhancement of the inversion and, consequently, an increase of the magnetic response. On the other hand, thermal treatments on highly disordered $ZnFe_2O_4$ almost erase its ferrimagnetic character (Fig. 1). The saturation magnetization M_S (Table 1, Fig. 3) was determined from the M linear behavior at magnetic fields $3 \leq H \leq 5$ T measured at 5 K [4]. Susceptibility results showed that the samples are in a superparamagnetic regime at high temperatures [9], while the blocking temperature T_B (Table 1) increases with D except for the thermally treated sample 2ZF10H-T. In the latter, even though the grain size has increased and the inversion has been reduced by the thermal treatment, residual magnetic clusters might dominate its magnetic behavior [9].

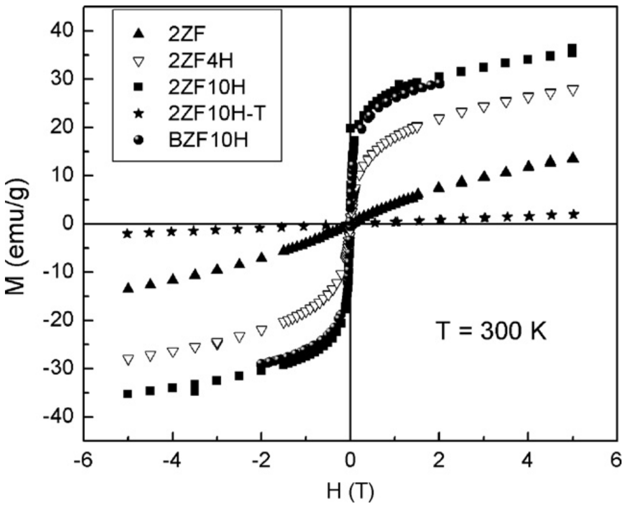

Fig. 1. Hysteresis loops M–H measured at 300 K.

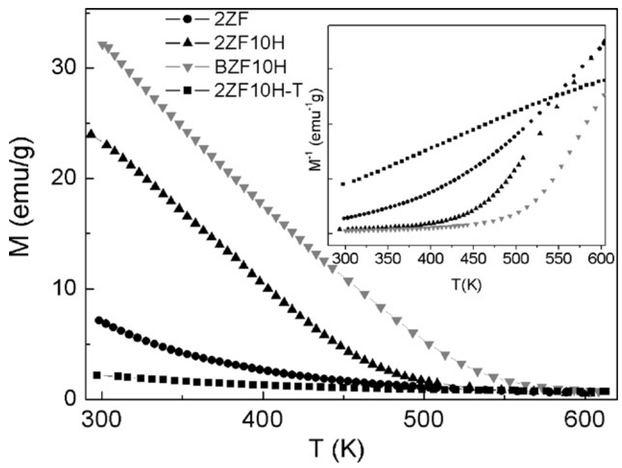

Fig. 2. Thermal dependence of the magnetization on warming from 298 to 610 K of nanocrystalline $ZnFe_2O_4$ with different sizes and degrees of inversion. Inset: thermal dependence of the reciprocal magnetization (M^{-1} *vs.* T).

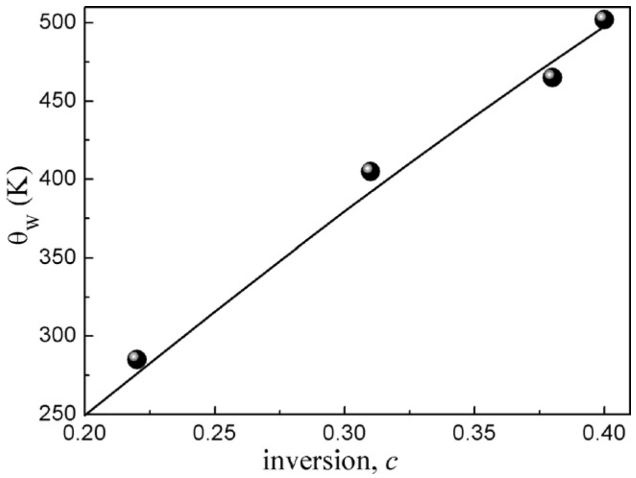

Fig. 3. Curie–Weiss temperature θ_W *vs.* inversion parameter. The solid line represents θ_W predicted by the Gilleo's model [14].

Fig. 2 shows the thermal dependence of the magnetization above 298 K. The maximum temperature achieved (610 K) was selected to avoid surpassing the stability region of the disordered state [8] and, at the same time, to include a region where the net magnetization was negligible. Furthermore, to minimize the thermally activated cation redistribution, the samples were first warmed up to 600 K and cooled down to room temperature and the magnetization was taken during a second running up to 610 K. Indeed, throughout *in situ* X-ray absorption experiments we found that the thermally activated relocation of Zn^{2+} ions from non-equilibrium to equilibrium positions occurs at about 600 K for 2ZF10H [8].

The disordered ferrites have a net magnetization below temperatures in the 400–510 K range (Fig. 2). The reciprocal magnetization, $M^{-1}(T)$, deviates from the linear behavior showed at high temperatures from different temperatures that depend on the degree of inversion (inset Fig. 1.). Conversely, M^{-1} for the thermally treated sample 2ZF10H-T decreases monotonically. M^{-1} extrapolates to zero at Curie–Weiss temperatures θ_W shown in Table 1. The positive sign of θ_W indicate the ferrimagnetic nature of the interactions amongst Fe^{3+} moments, whose effective strength increases with

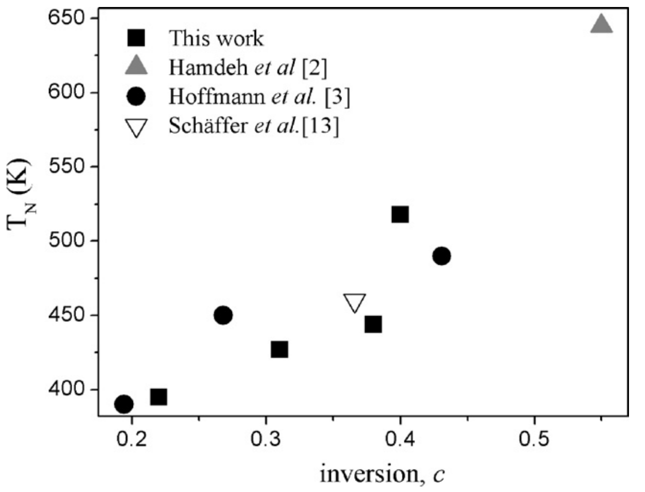

Fig. 4. Néel temperatures T_N determined by the intersection between the linear fit of the decrement of M and the region where M is negligible. T_N values taken from the literature are also included [2,3,13].

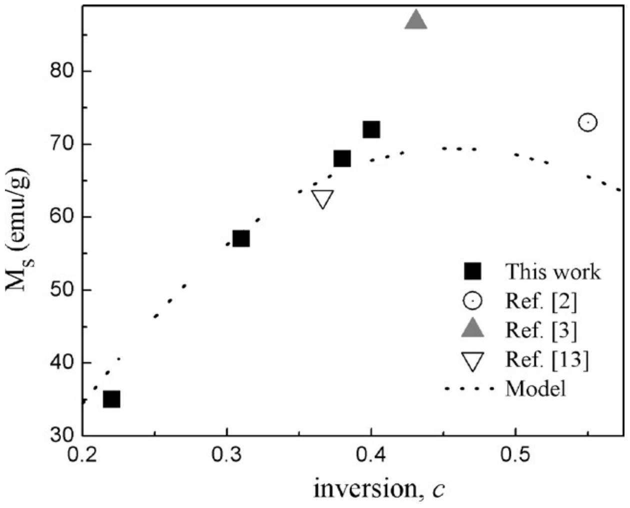

Fig. 5. Plot showing the saturation magnetization (M_S) as a function of the degree of inversion (c). Calculated M_S values obtained using Gilleo's model [14] are also included.

the inversion (Fig. 3). Cations in the disordered state probably distribute inhomogeneously, thus T_N might not be univocally defined and then a distribution of T_N might exist. Considering this, we report an effective temperature T_N (Table 1, Fig. 4) given by the intersection between the linear fit of the decrement of M and the region where M is negligible (Fig. 1).

Previous investigations on Ni and Mn-ferrites [10,11] showed that as D decreases T_N shifts towards lower values following a scaling law due to finite size effects. On the contrary, for the mixed ferrite $Ni_{0.5}Zn_{0.5}Fe_2O_4$, T_N was found to increase with the grain size reduction [12]. The latter was interpreted as due to the substitution of nonmagnetic Zn^{2+} ions by magnetic Ni^{2+} or Fe^{3+} at A sites that reinforces the strength of J_{AB} interactions and as a result T_N enhances. In our case, a simple scaling law that relates the T_N dependence with D is not suitable to describe the observed behavior. It seems that the inversion plays a more significant role in the T_N variation (Fig. 4). This can be interpreted as due to the lack of correlation between size and inversion that occurs in $ZnFe_2O_4$ [4], in addition to the T_N dependence on the J_{AB} interaction strength.

To estimate the expected variation of M_S and θ_W with the inversion parameter, we have calculated these values assuming a random distribution of superexchange interactions, as proposed a long time ago by Gilleo [14] for garnets and ferrimagnetic spinels. Figs. 3 and 5 show the results of these calculations for stoichiometric $ZnFe_2O_4$ [4]. We observe that the predicted results are in good agreement with our experimental findings. This hypothesis also agrees with our previous interpretation of the glassy magnetic behavior of these ferrites, which were interpreted through the interacting magnetic clusters formed due to the random non-equilibrium distribution of cations.

Acknowledgments

Financial support by CONICET (PIP 6524, PIP 6075); ANPCyT Argentina (PICT 38337) is acknowledged. SJS is member of Carrera del Investigador, CONICET, Argentina.

References

[1] K. Kamazawa, Y. Tsunoda, H. Kadowaki, K. Kohn, Phys. Rev. B 68 (2003) 024412.
[2] H.H. Hamdeh, et al., J. Appl. Phys. 81 (1997) 1851–1857.
[3] M. Hoffman, S.J. Campbell, H. Ehrardt, R. Feyerherm, J. Mater. Sci. Lett. 39 (2004) 5057–5065.
[4] S.J. Stewart, S.J.A. Figueroa, J.M. Ramallo López, S.G. Marchetti, J.F. Bengoa, R.J. Prado, F.G. Requejo, Phys. Rev. B 75 (2007) 073408.
[5] J.H. Shim, et al., Phys. Rev. B 73 (2006) 064404.
[6] G.F. Goya, H.R. Rechenberg, J. Magn. Magn. Mater. 196–197 (1999) 191.
[7] S.W. Lee, S. Bae, Y. Takemura, E. Yamashita, J. Kunisaki, S. Zurn, C.S. Kim, IEEE Trans. Magn. 42 (2006) 2833–2835.
[8] S.J.A. Figueroa, S.J. Stewart, J. Synchrotron Rad. 16 (2009) 63–68.
[9] H.M. Widatallah, I.A. Al-Omari, F. Sives, M.B. Sturla, S.J. Stewart, J. Magn. Magn. Mater. 320 (2008) e324–e326.
[10] C.N. Chinnasamy, A. Narayanasamy, N. Ponpandian, R. Justin Joseyphus, B. Jeyadevan, K. Tohji, K. Chattopadhyay, J. Magn. Magn. Mater. 238 (2002) 281.
[11] J.P. Chen, et al., Phys. Rev. B 54 (1996) 9288–9296.
[12] N. Ponpandian, A. Narayanasamy, C.N. Chinnasamy, N. Sivakumar, J.M. Greneche, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, Appl. Phys. Lett. 86 (2005) 192510.
[13] W. Shäffer, et al., Mater. Sci. Forum 321–324 (2000) 802–807.
[14] M.A. Gilleo, J. Phys. Chem. Solids 13 (1960) 33–39.